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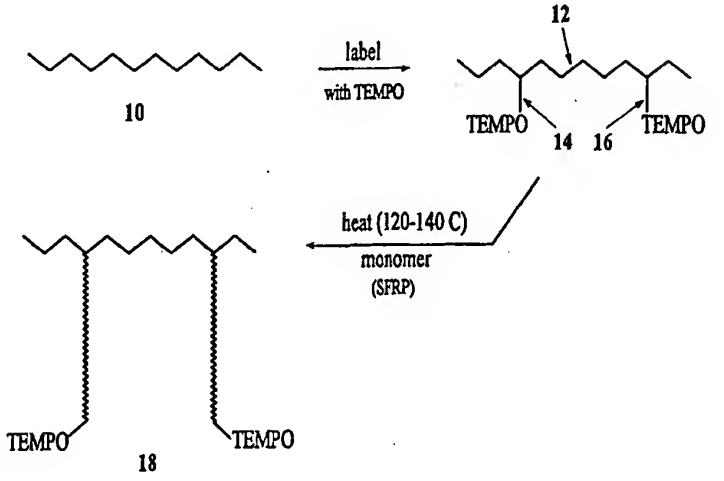
(54) **PROCEDE DE POLYMERISATION AVEC GREFFAGE**
(54) **GRAFT POLYMERIZATION PROCESS**



(57) Graft copolymers having side chains or branches of substantially uniform length and molecular weight are prepared by a process in which the backbone polymer is treated to create carbon centered free radicals thereon, e.g. by radiation, in the presence of a stable free radical compound. The free radical sites bond to the stable free radical through thermally labile bonds, so that heating of the "labelled" polymer in the presence of polymerizable monomer causes re-formation of the carbon centered free radicals with dissociation of the polymer-stable free radical compound bond, to effect graft copolymerization of the monomer. Controlled polymerization takes place by repetition of the three steps (dissociation, monomer addition, re-association) to give a graft copolymer with substantially uniform branch chains, each capped with a stable free radical group.

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CANADA

TO WHOM IT MAY CONCERN:

BE IT KNOWN that we GUILLET, James E., Canadian citizen of 31 Sagebrush Lane, Don Mills, Ontario, Canada, M3A 1X4 and BURKE, Nicholas A.D., Canadian Citizen of 12 Tally Ho Road, Dundas, Ontario, Canada, L9H 3M6, have invented certain new and useful improvements in

GRAFT POLYMERIZATION PROCESS

of which the following is a specification.

GRAFT POLYMERIZATION PROCESS

FIELD OF THE INVENTION

This invention relates to graft copolymers, and more particularly to processes for the preparation of graft copolymers of controlled molecular weight.

BACKGROUND OF THE INVENTION

Graft copolymers comprise a backbone polymer having a plurality of polymeric branches attached thereto, at different sites along the backbone polymer. The backbone polymer and the graft polymer may be comprised of one or more monomers, and may be of the same or a different chemical constitution from one another. By using different combinations of monomers for the backbone polymer and the graft polymer, copolymers having interesting combinations of properties can be prepared. High impact polystyrene is an example of a graft copolymer, in which a rubbery polymer such as polybutadiene is used as the backbone polymer and styrene is grafted thereon as branch chains of polystyrene. The presence of the rubbery backbone polymer confers on the resulting high molecular weight product a significantly increased impact strength, as compared with homopolymeric polystyrene, so that the resultant product has a combination of properties derived from the individual constituents.

Graft copolymers are commonly made by free radical initiated, solution, suspension or bulk polymerization. The preformed backbone, is mixed with the grafting monomer or monomers, and subjected to the action of free radicals which cause the development of grafting sites on the

backbone polymer chains and polymerization of the grafting monomers onto the grafting sites. Such a process is, however, random and uncontrolled, except within very broad ranges. The resulting graft copolymer has a non-homogeneous composition, with graft chains of widely varying molecular weight and length, and including non-grafted homopolymers and copolymers of the grafting monomers. Whilst such a non-homogeneous polymeric product is suitable for many applications, there are instances where a more homogeneous product, of pre-determined molecular weight and having the graft copolymer (branches) thereof of generally consistent length and molecular weight, is desirable.

It is an object of the present invention to provide a graft polymerization process which allows control over the length and molecular weight of the graft polymer branches which are formed.

SUMMARY OF THE INVENTION

The process of the present invention takes advantage of the properties of stable free radicals in effecting graft copolymerization onto a preformed polymeric backbone. In the process, the backbone polymer is caused to react with molecules of a stable free radical, to attach them to the backbone, at locations to act as potential grafting sites. Stable free radicals have the property of existing, in free radical form, in solution at ordinary room temperatures for extended periods of time. They do not react with themselves, or with other oxygen-centered free radicals, to any significant degree, and hence can exist in solution in relatively high concentrations. They will,

however, readily react with carbon-centered free radicals, for example, with polymer-centered free radicals.

Thus, the creation of free radical sites on the backbone polymer of a potential graft copolymer, in solution or suspension, or on the surface of said polymers, containing stable free radicals, will cause the stable free radicals to attach to the backbone polymer at the free radical sites. These are the potential grafting sites in the formation of the graft copolymer.

The linkage between the backbone polymer and the stable free radical is thermally labile. Accordingly, when the backbone polymer-stable free radical combination is appropriately heated, in solution or suspension containing the graft monomer or monomers, the linkage can undergo a reversible dissociation. Dissociation of the backbone polymer-stable free radical linkage leaves carbon-centered free radicals on the polymer which initiate graft polymerization of the graft monomer or monomers onto these free radical sites, with the free radical becoming dispersed on the growing polymer chain end. The free radical at the distal end of the graft chain will recombine with the stable free radical, in a step which is the reverse of the dissociation step. As heating continues, the stable free radical may be dissociated again, at which time the graft chain may be extended by the incorporation of additional monomer units. Repetition of these three steps (dissociation, addition of monomer, re-association of stable free radical) during heating leads to slow and controlled growth of the side chains. The growth of the graft chains is an example of a stable free radical polymerization (SFRP). By adjustment of the heating time, along with appropriate choice of graft monomer

concentration, the length and molecular weight of the graft polymer chain can be controlled. Moreover, substantial uniformity between the graft copolymer chains as regards their length and molecular weight can be achieved. The total molecular weight of the graft copolymer will also depend on the number of grafting sites per backbone polymer.

Thus, according to the present invention from one aspect, there is provided a process for preparing graft copolymers having graft chains of controlled molecular weight, which comprises:

preparing a solution or dispersion or solid surface of a preformed backbone polymer;

creating free radical sites on the backbone polymer;

chemically attaching stable free radicals to said free radical sites;

effecting controlled graft polymerization at the sites of attachment of said stable free radicals by changing the solution conditions so as to cause dissociation of the stable free radical attachments with formation of free radical sites at the sites of attachment, in the presence of a free radical polymerizable monomer;

effecting free radical graft polymerization of graft monomer onto said free radical sites to form graft polymer chains, with the stable free radical chemically attached to the distal end.

BRIEF REFERENCE TO THE DRAWINGS

Figure 1 of the accompanying drawings is a diagrammatic representation of the scheme for preparing graft copolymers according to the invention;

Figures 2, 3, 4 and 5 are presentations of the results of GPC analysis of the various products prepared according to Example 1 described herein;

Figures 6 and 7 and GPC chromatograms of products of Example 2 below;

Figures 8 and 9 are GPC chromatograms of products of Example 3 below;

Figure 10 is a GPC chromatogram of the product of Example 4 below.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Suitable backbone polymers for the present invention include substantially any polymer on which carbon-centered free radical sites can be generated. The polymers include hydrocarbon polymers including polyethylene, polypropylene, polystyrene, polybutylene, other polyolefins and the like, and unsaturated hydrocarbon polymers such as polybutadiene, polystyrene, polyisoprene; copolymers of hydrocarbon monomers such as ethylene-propylene copolymers and ethylene-propylene-diene terpolymers (EPDM), polymers of vinyl group monomers containing functional groups such as polyacrylic acid, polymethacylic acid, polyacrylates, polymethacrylates, copolymers thereof such as poly(ethylene-vinyl acetate), carbohydrate polymers such as

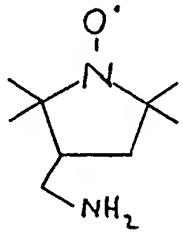
celluloses, starches, nucleic acids and dextran; polyesters; polyamides; polypeptides; and the like. One of the advantages of the present invention lies in the fact that it can be worked with backbone polymers containing normally unreactive functional groups.

Free radical sites on the backbone polymers can be prepared, according to the process of the present invention, by a variety of different techniques. For example, they can be prepared radio chemically - the passage of gamma rays (from a cobalt-60 source for instance) through a sample will create a number of radical species. They can be prepared photochemically, e.g. by irradiation of a suitable compound (benzophenone, anthraquinone, polymerization photoinitiator) to produce species (radicals, excited states) capable of H-abstraction from the polymer chain. They can be produced chemically, using systems such as Fenton's reagent (Fe^{2+}/H_2O_2) and polymerization initiators (benzoyl peroxide, AIBN, per-sulfate) to produce radicals capable of hydrogen abstraction.

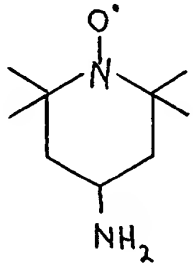
The process of the present invention creates the free radical sites on the backbone polymer in solution or at the surface of a solid polymer, and chemically attaches stable free radicals to these free radical sites. Oxygen centered radicals are preferably used as the reactive radicals in the chemical process for producing free radicals on the polymer backbone chain, because stable free radicals react rapidly with carbon-centered radicals but not with most oxygen-centered radicals. Accordingly, radicals derived from compounds such as hydrogen peroxide, benzoyl peroxide and anthraquinone will be oxygen-centered and less likely to react with the stable free radical.

The stable free radicals useful in the present invention are thus those which can exist in solution for at least 24 hours in free radical form, without recombining with one another to any substantial extent. They are highly reactive with carbon-centered free radicals, but substantially unreactive with oxygen-centered free radicals, and accordingly are derived from oxygen-centered free radical generating compounds themselves. They are known in the art, and representative ones of them are commercially available. The most common type of stable free radicals are aminoxyl radicals (also known as nitroxyl radicals or nitroxides), examples of which include:

3-aminomethyl-PROXYL (AMP) of chemical formula:

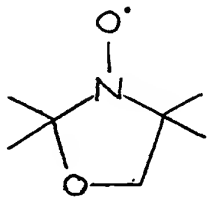


4-amino-TEMPO (AT), of chemical formula:



and

DOXYL, of chemical formula:



Graftable comonomers for use in the present invention include substantially any monomer which can be polymerized by free radical mechanisms, in solution or suspension. They include styrene, ethylene, propylene, butylene, butadiene, isoprene, isobutylene, vinyl acetate, acrylic acid, methacrylic acid, methylmethacrylate, vinyl chloride and the like, and combinations of 2 or more such monomers.

The process of the present invention, in its preferred embodiment, proceeds by first attaching to the backbone polymer a stable free radical compound, by subjecting the backbone polymer to free radical creating conditions in the presence of the stable free radical compound. The bond between the free radical compound and the polymer backbone so formed is thermally labile, so that, by heating the solution of the polymer-stable free radical complex above a temperature of, for example, 110°C, this stable free radical compound dissociates from the polymer backbone, leaving carbon-centered free radical site on the polymer. This takes place in the presence of the graft polymerizable monomer or monomers, and upon this creation of the polymer backbone free radical site, graft copolymerization takes place at that site by the SFRP mechanism described previously. In common with all other free radical polymerization processes, the free radical element remains

at the distal end of the growing graft polymer chain. The length of the graft copolymer branches is controlled by the length of time between the elevation in temperature to split off the stable free radical molecule, and the subsequent reduction in temperature to render the stable free radical molecule inactive. By this means, control of the polymerization time and temperature controls the copolymer branch length, all such copolymer branches being substantially uniform in length and molecular weight.

The graft copolymer is subsequently isolated from excess, unpolymerized monomer by conventional means, e.g. precipitation.

Since the side chains of the graft copolymer bear a stable free radical group at the distal end of each chain, it is possible to further extend the side chain, if so desired. Treating the graft copolymer under SFRP conditions will cause lengthening of the side chain where the new section of the side chain may be composed of the same monomer(s) used in the initial grafting process or different ones.

Figure 1 of the accompanying drawings shows diagrammatically a pre-formed backbone polymer 10 which, in a first "labelling" step, is treated to create carbon-centred free radicals in the presence of the stable free radical compound TEMPO. This produces a "labelled" backbone polymer 12, with stable free radical TEMPO groups covalently bonded thereto through thermally labile bonds 14, 16, etc. On heating to a temperature, preferably in the 120-140°C range, these bonds dissociate creating free radicals at the positions of dissociation on the backbone polymer chains. This heating takes place in the presence

of monomer, which polymerizes by a free radical mechanism from the carbon centred free radicals so formed on the backbone polymer chain. The graft polymerization proceeds slowly until terminated by re-attachment of the TEMPO stable free radicals to the growing polymer chains, with each such graft polymer chain growing substantially evenly in length, to produce graft copolymer 18.

The process of the present invention is further illustrated in the following specific examples.

EXAMPLE 1 - PHOTOCHEMICAL TREATMENT OF BACKBONE POLYMERS TO ATTACH STABLE FREE RADICALS THERETO

Poly(acrylic acid) (90,000 g/mol; 0.102 g), 2,6-anthraquinone disulfonate, disodium salt (AQDS) (4.3 mg) and amino-TEMPO (AT)(10.0 mg) were dissolved in 10 ml of water. The solution was placed in a quartz tube, deoxygenated by bubbling with nitrogen for 10 minutes, and then irradiated in a Rayonet RPR-100 photoreactor (16 x 300 nm lamps). Samples (3 mL) taken before irradiation and after 40 minutes irradiation were adjusted to pH greater than 7 with NaOH solution or pH 10 buffer before the addition of 0.6 ml of 0.09% (w/v) fluorescamine in acetonitrile. The solutions were transferred to dialysis tubing (Spectra-Por, 12-14,000 molecular weight cut off) and exhaustively dialysed with water. The purified polymer solutions were then analysed by UV/visible spectroscopy and gel permeation chromatography (GPC).

For this analysis, aqueous samples were analysed with a Waters GPC(U6K injector, 6,000 A pump) equipped with a 30 cm Shodex KB806M column (hydroxylated PMMA packing, fractionation range 10^3-10^7), a Waters R401 differential

refractometer and an ABI 980 fluoroescence detector (Applied Biosystems Inc). The fluoroescamine/amine adduct was excited at 385 nm and a long pass filter (417 or 470 nm) was used to ensure that only emission from the fluorescamine/amine fluorophore reached the detector. UV/visible spectra were measured with a Hewlett-Packard HP 8451A spectrometer.

The same general photochemical procedure was used to generate polymer-centered radicals on several different polymers, as follows:

polyethylene oxide, 300 k
poly(acrylic acid), 90 k
dextran, 75 k
poly(sodium 4-styrene sulfate), PSSS, 200 k and 46 k
poly(vinylpyrrolidone), PV, 44k
deoxyribonucleic acid, DNA, ca. 200 k

Following binding of the AT group to the polymer chain, AQDS and excess AT were removed, fluorescamine was added and then small molecule impurities were removed by dialysis or ultrafiltration. Fluorescamine reacts with primary amines to produce highly fluorescent adducts, so that it acts as a convenient marker to demonstrate the coupling of the stable free radical compound to the polymer backbone.

Figure 2 attached hereto is the GPC chromatogram for polyacrylic acid irradiated in the Rayonet for 0 or 40 mins. in the presence of AQDS/AT in water, and then reacted with fluorescamine. A refractive index (RI) peak 20 and a fluorescence peak 22 are clearly demonstrated for the irradiated samples, showing successful binding of AT to the polymeric backbone. In addition, the irradiated sample

displays an absorption at 385 nm in the UV-visible spectrum typical of the fluorescamine-amine adduct. This absorption is absent from the spectrum of the unirradiated sample.

Figure 3 is a similar spectrum of the photochemically-treated dextran(75,000 g/mol). It shows an essentially similar result, with an RI peak 24 and a fluorescence peak 26, indicating that the stable free radical AT has successfully attached to the polymer backbone by a free radical mechanism, so that the polymers are now appropriate backbone polymers for grafting according to the present invention.

Following essentially similar features, poly(sodium styrene sulfonate) (200,000 g/mol) has been successfully joined to stable free radical AT, using both AQDS and AQMTEA (2-anthraquinonylmethyl triethylammonium bromide) as photochemical H-abstractor, and fluorescamine as fluorescent marker. The resulting polymers were also similarly suitable for use as a grafting backbone in the present invention. Their spectra showed evidence of binding of the stable free radical compound to the polymer backbone.

In parallel experiments, various backbone polymers (polystyrene and PMMA) were photochemically irradiated in organic solution (benzene) in the presence of anthraquinone (AQ) or t-butylperoxide ($(t\text{-}BuO)_2$) as free radical generators, and in the presence of AT. Following irradiation a fluorescent marker (BODIPY-FL, SE) was added and spectral evidence of the binding of the stable free radical compound to the backbone polymer was obtained (Figures 4 and 5), showing that they are appropriate for the use as backbone polymers in graft copolymer preparation

according to the invention. Peak 28 on Figure 4 is from the RI signal, peak 30 on Figure 4 from the fluorescence signal. Peak 32 on Figure 5 is from the RI signal, peak 34 from the fluorescence signal. The absence of evidence for degradation or cross-linking of the polymers in Figures 2-5 is also noteworthy.

In addition, polypropylene membranes immersed in benzene solutions of AT and either 2-methylanthraquinone or t-butyl peroxide were irradiated (300 nm). The membranes were washed thoroughly, reacted with BODIPY-FL, SE (4,4-difluoro-5,7-dimethyl-4-bora-3a,4a-diaza-s-indacene-3-propionic acid, succinimidyl ester; (Molecular Probes), and then washed again. Fluorescence spectroscopy (SLM 4800S spectrofluorimeter) revealed BODIPY-FL emission (λ_{ex} = 495 nm; λ_{em} = 512 nm) from the surface of the irradiated membranes but not from control samples. This demonstrates that AT was bound to the surface of the membranes and that it is possible to prepare solid polymer surfaces so that they are suitable for grafting. Since this is done photochemically it leads to the possibility of making graft polymer images on plastic films. These could be doped to provide electrical conductivity and other electro-optical properties to the photoinduced patterns.

EXAMPLE 2 - RADIOCHEMICAL TREATMENT OF BACKBONE POLYMERS TO ATTACH STABLE FREE RADICALS THERETO

Polystyrene (280,000 g/mol; 0.169 g) and AT (0.256 g) were dissolved in 25 mL benzene. 5 mL of this solution was transferred to each of four Pyrex tubes. The samples were degassed by three freeze/pump/thaw cycles before the tubes were sealed. The samples were exposed to 0, 0.5, 1 or 2 Mrads of γ-rays from a ^{60}Co source. The polymers were

precipitated in methanol, filtered, washed with methanol and then air dried. Each polymer sample was dissolved in benzene (1 mL) before the addition of 1 drop of pH 10 buffer and 100 μL of 12.8 mM BODIPY-FL, SE in DMSO. The solutions were mixed on a vortex mixer and then stored at room temperature for 1 hour. The polymer was precipitated in methanol (50 mL), filtered, washed with methanol and then purified by a second precipitation from benzene into methanol. The polymer samples were dried in a vacuum oven (45°C for 2 hours) and then dissolved in THF prior to analysis by GPC.

The organic soluble samples were analysed using a Waters GPC (U6K injector, 510 pump) equipped with two 30-cm Zorbax PSM columns (60S and 1000S), a Waters R401 differential refractometer and an ABI 980 fluorescence detector. BODIPY-FL was excited at 500 nm and a 515 nm long pass filter was used to filter the emission.

The exposure of polymers to gamma rays results in the creation of polymer-centered radicals, as is well known. Using GPC analysis, it was shown (Figure 6) that the polystyrene had been successfully attached to AT, following exposure to gamma rays. Similar experiments were conducted using as starting polymers poly(N-isopropylacrylamide) P(NIPAM), polyacrylic acid and DNA. Figure 7 appended hereto is the GPC chromatogram for the polyacrylic acid experiment described above, the different traces representing different exposure to gamma rays. The Figure shows that the polymer bears flurophores indicative of attachment of AT and that the degree of attachment is proportional to the dose of radiation.

EXAMPLE 3 - THERMAL TREATMENT OF BACKBONE POLYMERS TO ATTACH STABLE FREE RADICALS THERETO

In these experiments, chemical radical generating systems are used, such as peroxy compounds, for example hydrogen peroxide, persulfate, benzoyl peroxide, peroxide nitrite, which decompose thermally to produce radical species capable of creating radicals on the polymer chain by H-abstraction or addition. Polymer-centered radicals so formed, are efficiently scavenged by the spin trap provided by the stable free radical compound.

Three aqueous solutions were prepared by combining 20 μL of a 1.02% DNA solution (Sigma, single-stranded, denatured, co-migrates with 587-831 base pair marker fragments) and 400 μL of a 39.6 mM amino-TEMPO solution. The solutions were bubbled with nitrogen for 10 minutes and then 80 μL of hydrogen peroxide (0.75%, 3%, or 6%) was added with vigorous stirring. The samples were maintained at room temperature for 80 minutes.

The samples were purified by ultrafiltration in a microcentrifuge. The samples were transferred to centrifuge tubes equipped with ultrafiltration inserts (Gelman NanoSpin Plus, 30000 Molecular Weight Cut-Off). The samples were spun in a microcentrifuge (IEC MiniMax) at 10,000 rpm until the sample volume was reduced to about 20 μL. The retenate (which includes the polymer) was washed twice by adding water (500 μL) and spinning in the microcentrifuge until the retentate volume was about 20 μL. To the retentate in each ultrafiltration insert was added 100 μL of water, 75 μL of pH 10 buffer and 60 μL of 11.5 mM fluorescamine in acetonitrile. After 10 minutes the solution volume was reduced to about 20 μL by spinning in

the microcentrifuge. The retentate was washed 2 times with water. The final retentates were diluted with water to give a total volume of about 400 μL. The solutions were analysed by GPC as described in Example 1. The GPC data, shown in Figure 8, demonstrates the occurrence of efficient binding of AT to DNA which is proportional to the amount of hydrogen peroxide used, and that binding is achieved without degradation or cross-linking of the DNA. On Figure 8, curves 36 are from RI, curves 38 from fluorescence detectors.

Radical generating systems used include hydrogen peroxide (H_2O_2), Fenton's reagent (H_2O_2/Fe^{2+}), persulfate/heat, persulfate/tetramethyl-ethylenediamine and t-butylperoxide/heat. Specific individual polymers treated in this way with one or more of these systems were polyacrylic acid, poly(sodium styrene sulfonate), dextran, poly(vinylpyrrolidine), poly(2-vinylnaphthalene), and polyethylene oxide. Upon analysis as described, they exhibited fluorescence indicating successful attachment of the stable free radical compound to the polymer, indicating that the resultant polymer is suitable for use as a backbone polymer in the graft polymerization process of the present invention. For instance, Figure 9 shows the GPC chromatogram for poly(2-vinylnaphthalene) (100,000 g/mol) after heating (130°C, 2.5 h) in the presence of t-butylperoxide/AT in t-butylbenzene, and then reaction with BODIPY-FL, SE. The treated polymer displays a strong fluorescence peak 40 which is absent from the untreated polymer. Curves 42 are from RI detection.

EXAMPLE 4 - GRAFT COPOLYMERIZATION

PSSS (46,000 g/mL, MW standard) attached to stable free radical compound AT through the action of AQMTEA/AT/hν and purified by centrifugal ultrafiltration, as described in Example 3 above, was mixed in the amount of 10 mg with sodium styrene sulfonate (950 mg) and 80% ethylene glycol (4 mL) in a small two-necked flask. The solution was deoxygenated by bubbling with argon for 30 minutes and then heated in an oil bath at 135°C for 5 hours under an argon atmosphere. The polymer was precipitated in acetone/methanol (3:1) and then further purified by centrifugal ultrafiltration. The polymer was reacted with fluorescamine as described above and then purified by centrifugal ultrafiltration prior to analysis by GPC.

This experimental process is illustrated diagrammatically in Figure 1 of the accompanying drawings.

The purified graft copolymer from this Example was subjected to GPC analysis, using both fluorescence (F) and refractive index detectors, and the results are shown in Figure 10 of the accompanying drawings. Curves 44 (chain dots, consistent with earlier Figures) are from fluorescence detectors, curves 46 (solid lines, consistent with earlier Figures) are from RI detectors. The polymer gives a fairly sharp RI peak and elutes 1.5 minutes earlier than the ungrafted PSSS sample. Comparison with a calibration curve based on PSSS standards indicates a molecular weight increase from 46,000 to about 230,000 g/mol. GPC analysis of the ungrafted PSSS showed that each chain bore, on average, four AT groups, and thus, the molecular weight increase upon grafting corresponds to about 46,000 g/mol per graft on average. A strong

fluorescent peak which coincides with the RI peak is also observed. This shows that the higher molecular weight polymer bears AT groups and that the high molecular weight polymer is the result of grafting and not SSS auto-polymerization. Each grafted chain is believed to be capped with an AT group which might be used as a site to further extend the side chains with SSS or another monomer.

WE CLAIM:

A process for preparing graft copolymers having graft chains of controlled molecular weight, which comprises:

preparing a solution or dispersion or solid surface of a preformed backbone polymer;

creating free radical sites on the backbone polymer;

chemically attaching stable free radicals to said free radical sites;

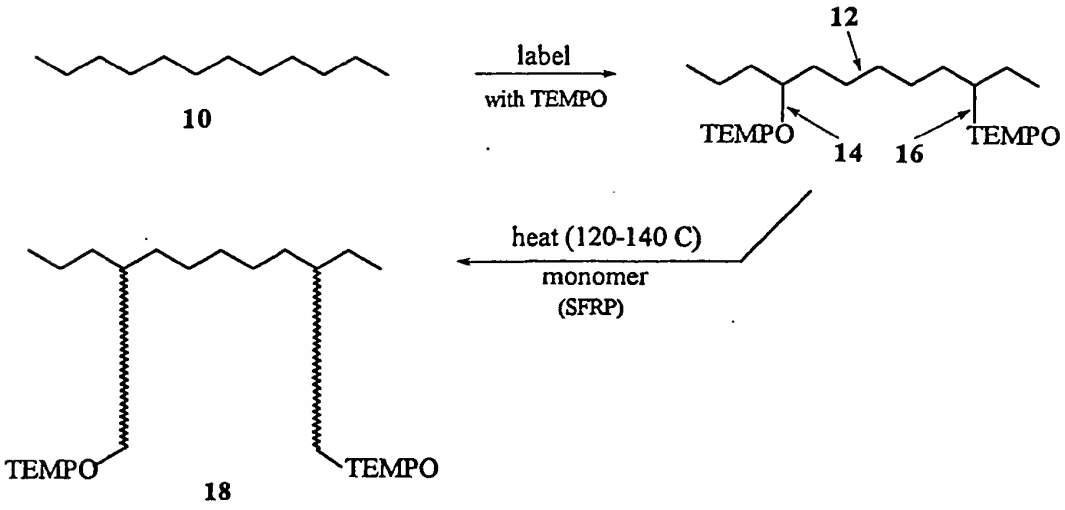
effecting controlled graft polymerization at the sites of attachment of said stable free radicals by changing the solution conditions so as to cause dissociation of the stable free radical attachments with formation of free radical sites at the sites of attachment, in the presence of a free radical polymerizable monomer;

effecting free radical graft polymerization of graft monomer onto said free radical sites to form graft polymer chains which are capped at the distal end of the stable free radical.

ABSTRACT OF THE DISCLOSURE

Graft copolymers having side chains or branches of substantially uniform length and molecular weight are prepared by a process in which the backbone polymer is treated to create carbon centered free radicals thereon, e.g. by radiation, in the presence of a stable free radical compound. The free radical sites bond to the stable free radical through thermally labile bonds, so that heating of the "labelled" polymer in the presence of polymerizable monomer causes re-formation of the carbon centered free radicals with dissociation of the polymer-stable free radical compound bond, to effect graft copolymerization of the monomer. Controlled polymerization takes place by repetition of the three steps (dissociation, monomer addition, re-association) to give a graft copolymer with substantially uniform branch chains, each capped with a stable free radical group.

Figure 1: Binding of TEMPO to backbone polymers and then growth of graft side chains by stable free-radical polymerization (SFRP).



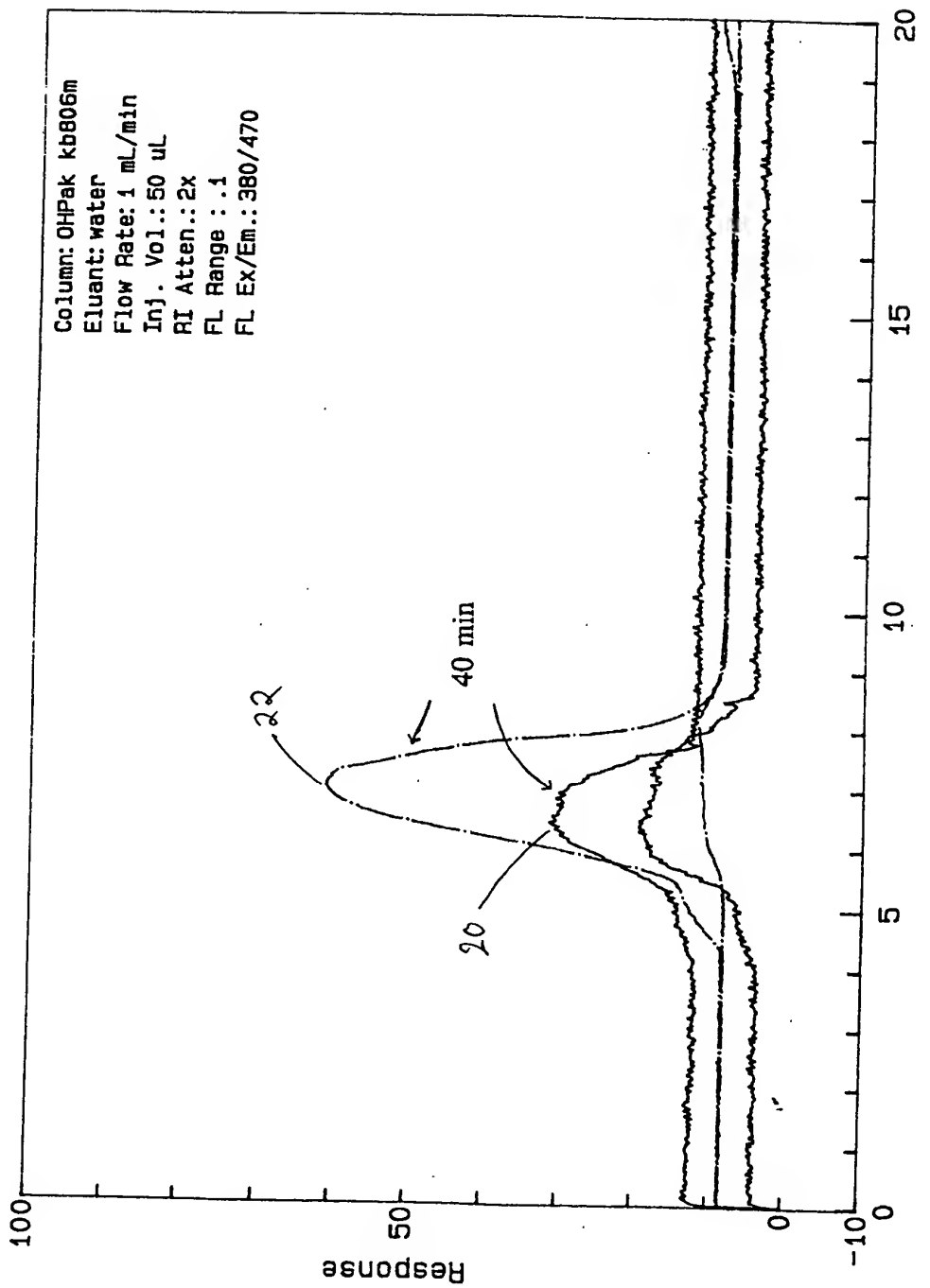


Figure 2: GPC chromatogram for polyacrylic acid (90,000 g/mol) irradiated in the Rayonet (300 nm) for 0 or 40 min in the presence of AQDS/AT in water, and then reacted with fluorescamine. Signals from the RI (purple) and fluorescence (red) detectors are shown.

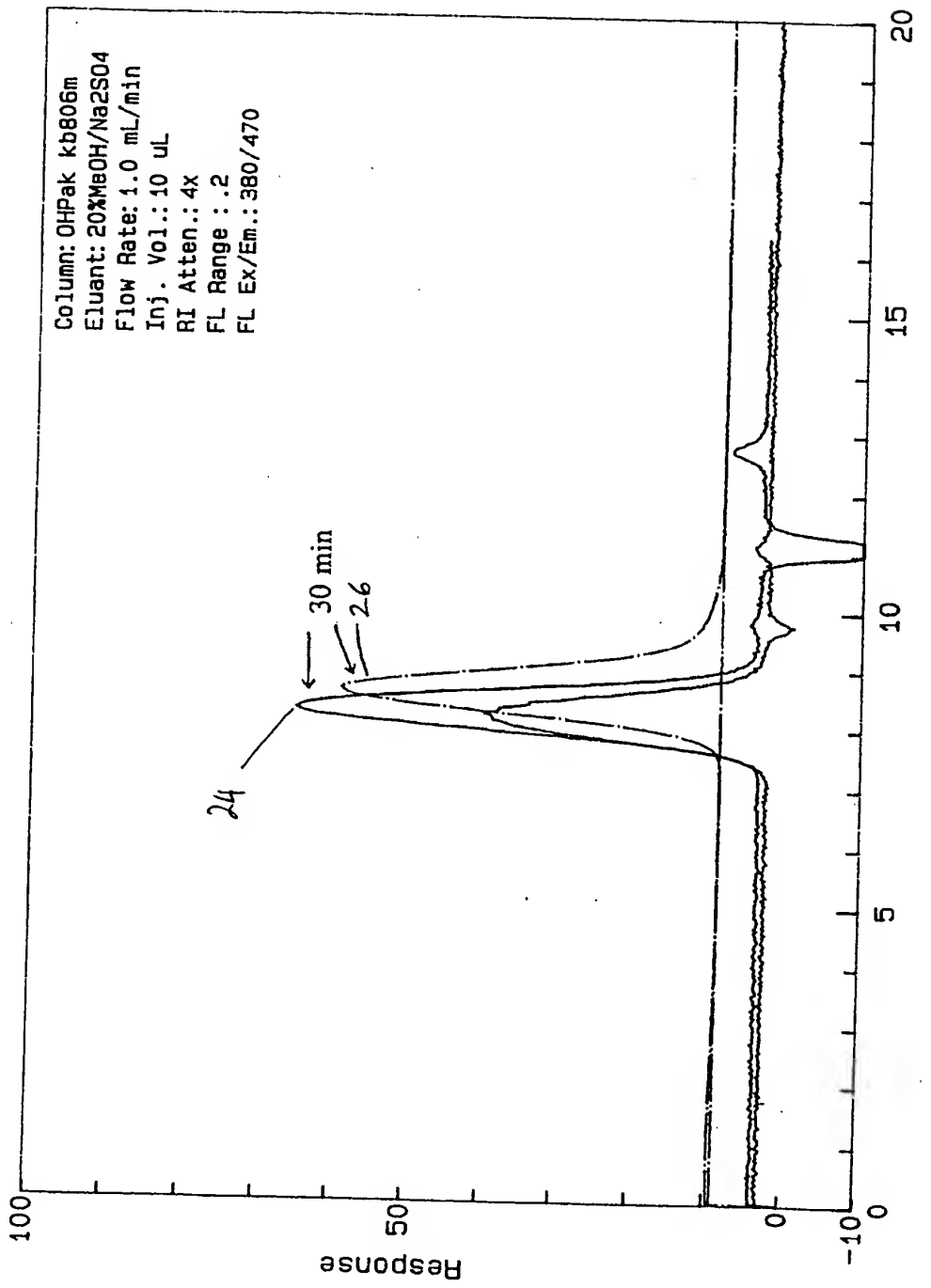


Figure 3: GPC chromatogram for dextran (75,000 g/mol) irradiated for 0 or 30 min with a sunlamp in the presence of AQDS/AT in water, and then reacted with fluorescamine. Signals from the RI (purple) and fluorescence (red) detectors are shown.

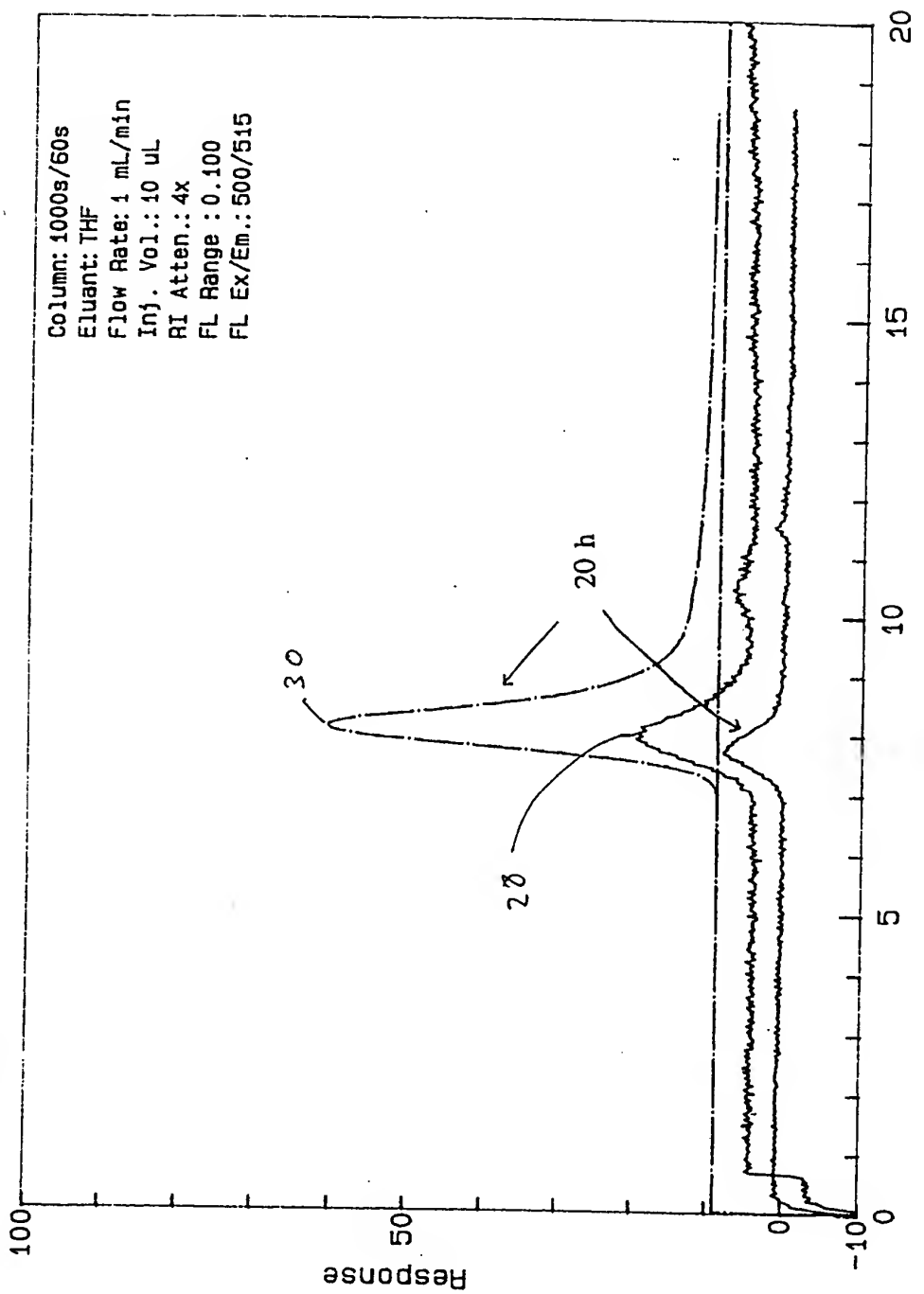


Figure 4: GPC chromatogram for PMMA (25,000 g/mol) irradiated for 0 or 20 h in the Rayonet (300 nm) in the presence of t-butyl peroxide/AT in benzene, and then reacted with BODIPY-FL, SE. Signals from RI (purple) and fluorescence (red) detectors are shown.

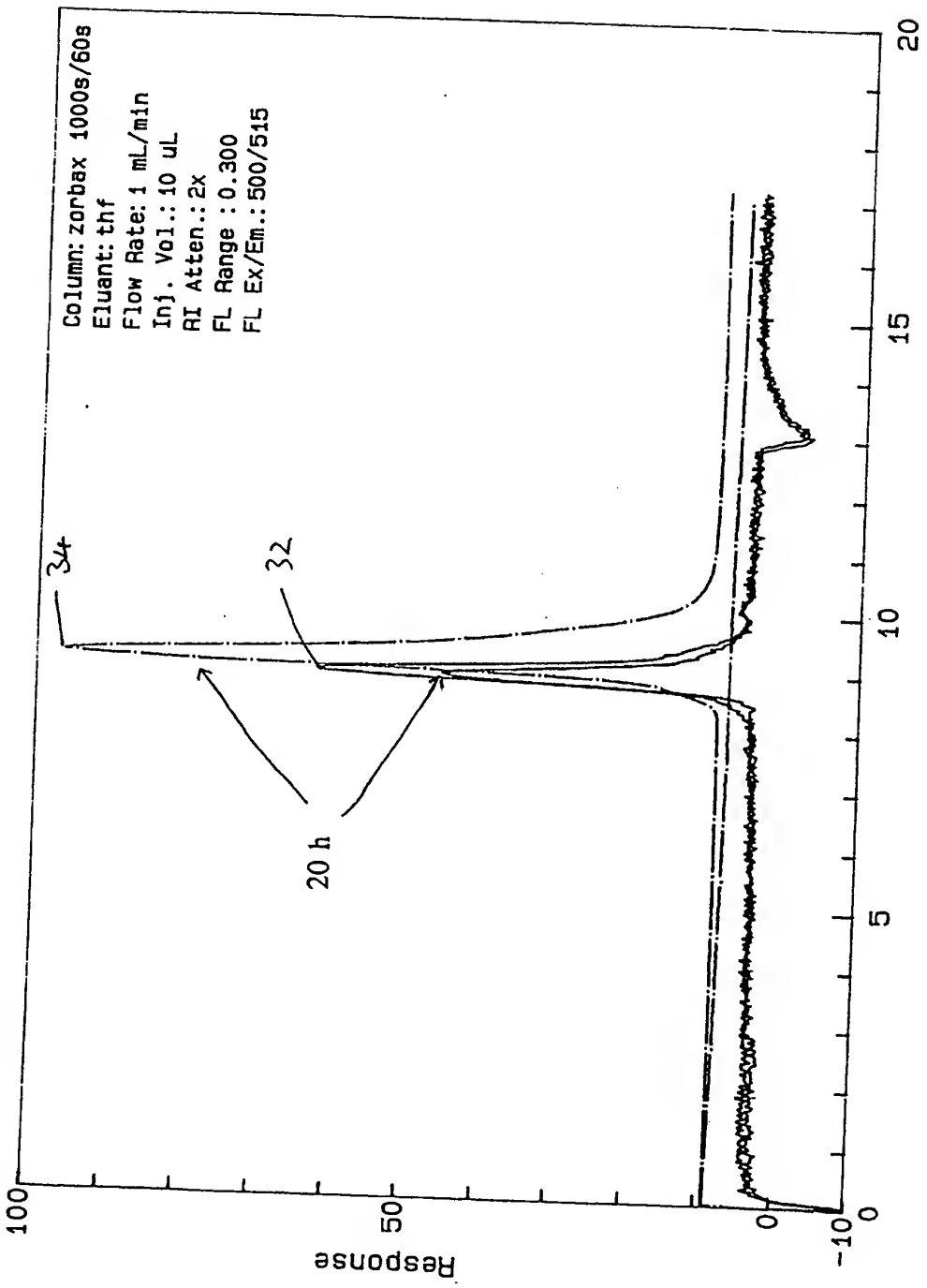


Figure 5: GPC chromatogram for PS (4,750 g/mol) irradiated for 0 or 20 h in the Rayonet (300 nm) in the presence of t-butyl peroxide/AT in benzene, and then reacted with BODIPY-FL, SE. Signals from RI (purple) and fluorescence (red) detectors are shown.

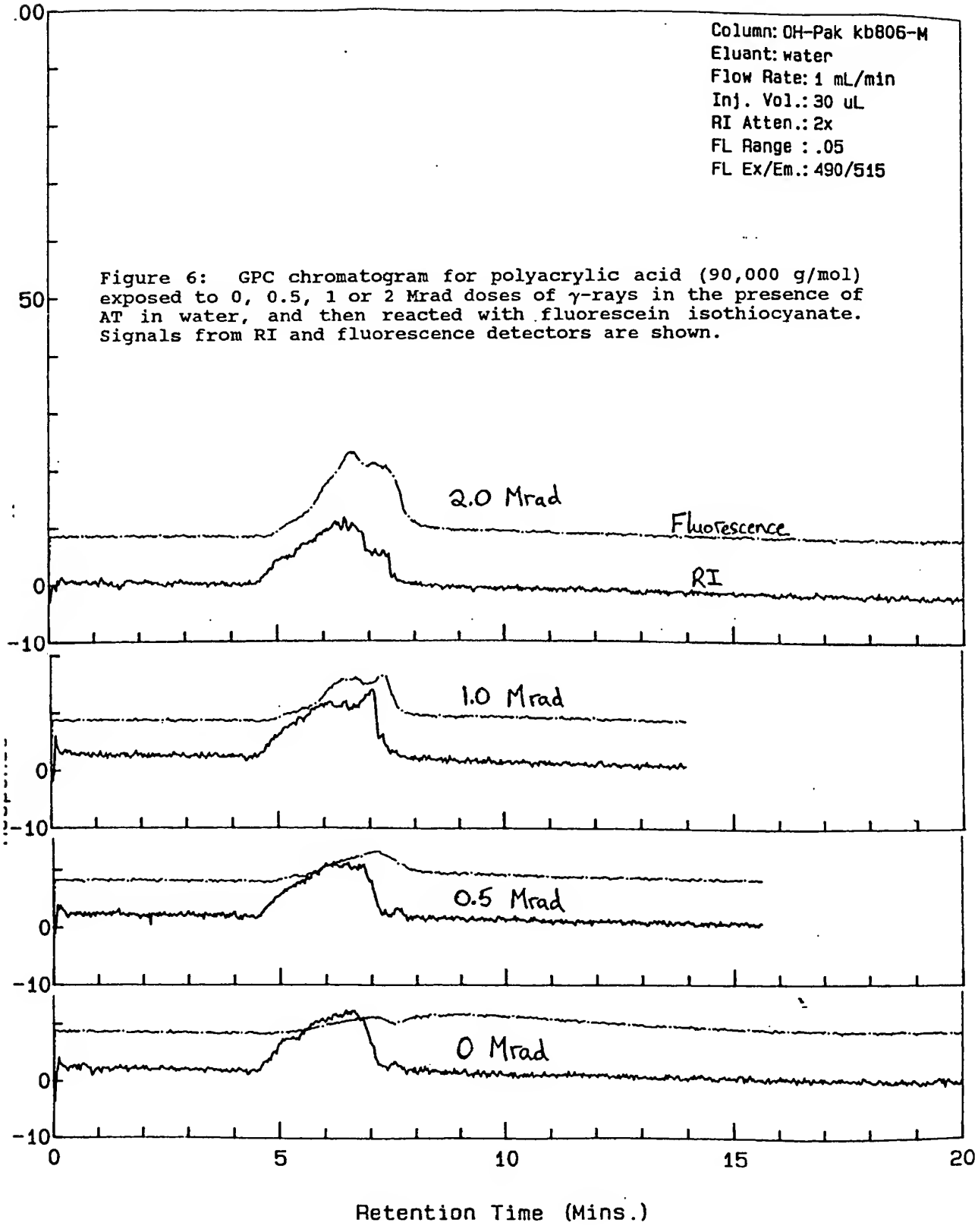


Figure 6: GPC chromatogram for polyacrylic acid (90,000 g/mol) exposed to 0, 0.5, 1 or 2 Mrad doses of γ-rays in the presence of AT in water, and then reacted with fluorescein isothiocyanate. Signals from RI and fluorescence detectors are shown.

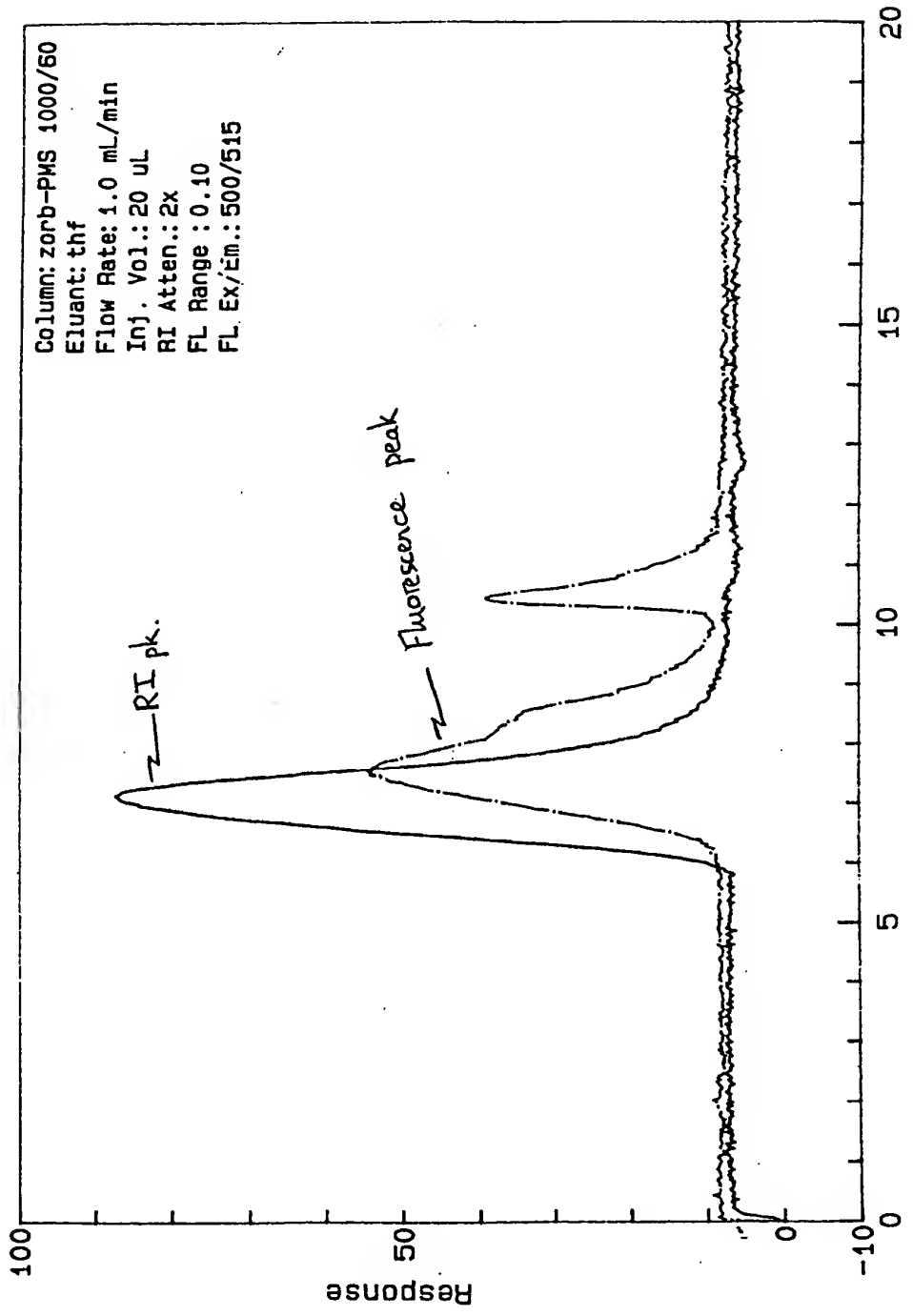


Figure 7: GPC chromatogram for PS (280,000 g/mol) exposed to 2 Mrad dose of γ-rays in the presence of AT in benzene and then reacted with BODIPY-FL, SE. Signals from RI and fluorescence detectors are shown.

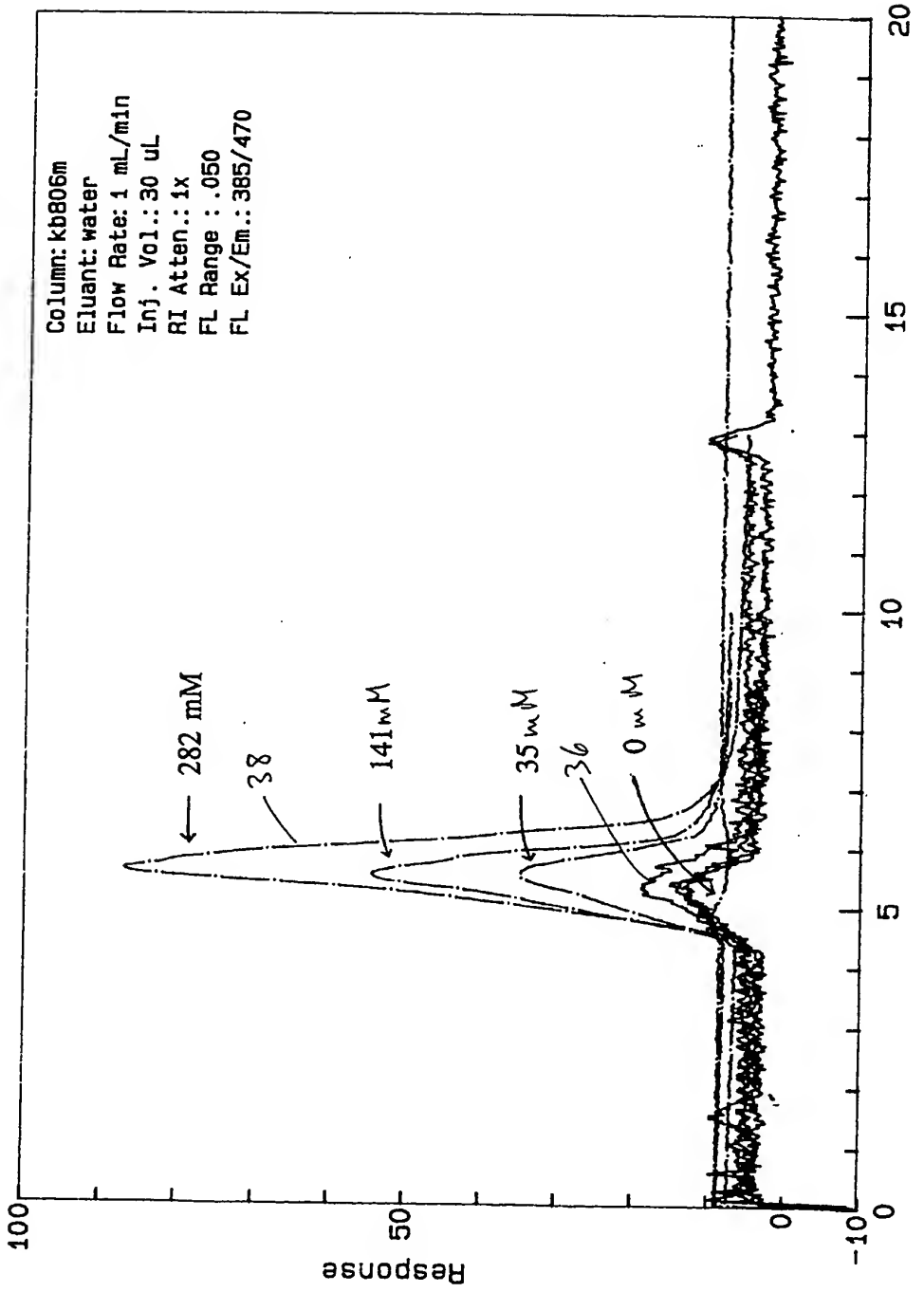


Figure 8: GPC chromatogram for DNA (≈200,000 g/mol) treated with 0, 35, 141 or 282 mM H_2O_2 and AT at room temperature in water, and then reacted with fluorescamine. Signals from RI (purple) and fluorescence (red) detectors are shown.

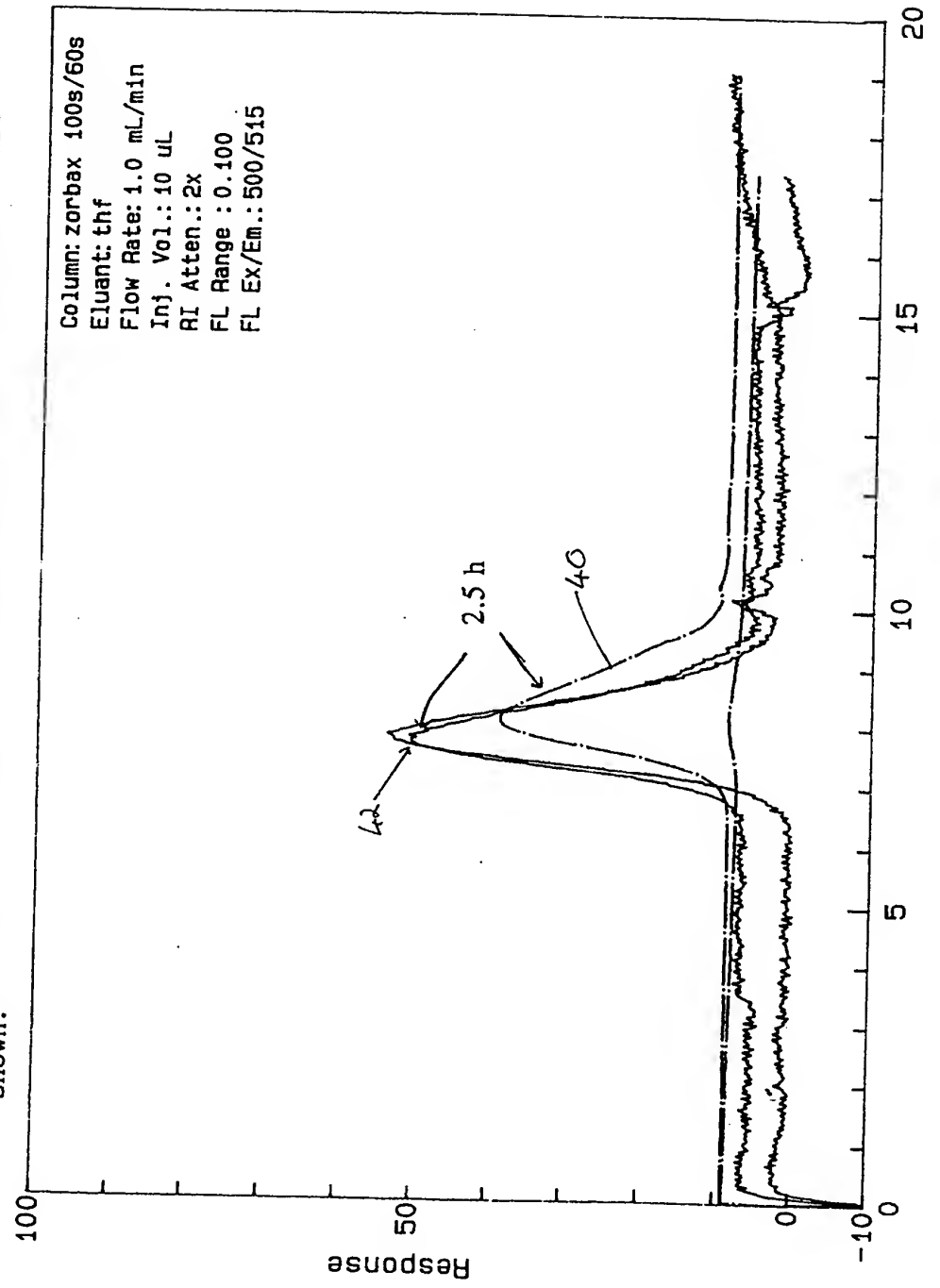


Figure 9: GPC chromatogram for poly(2-vinylnaphthalene) (100,000 g/mol) treated with t-butylperoxide/AT for 2.5 h at 130 °C in t-butylbenzene, and then reacted with BODIPY-FL, SE. For comparison, the GPC trace for an untreated sample of polymer is also shown. Signals from RI (purple) and fluorescence (red) detectors are shown.

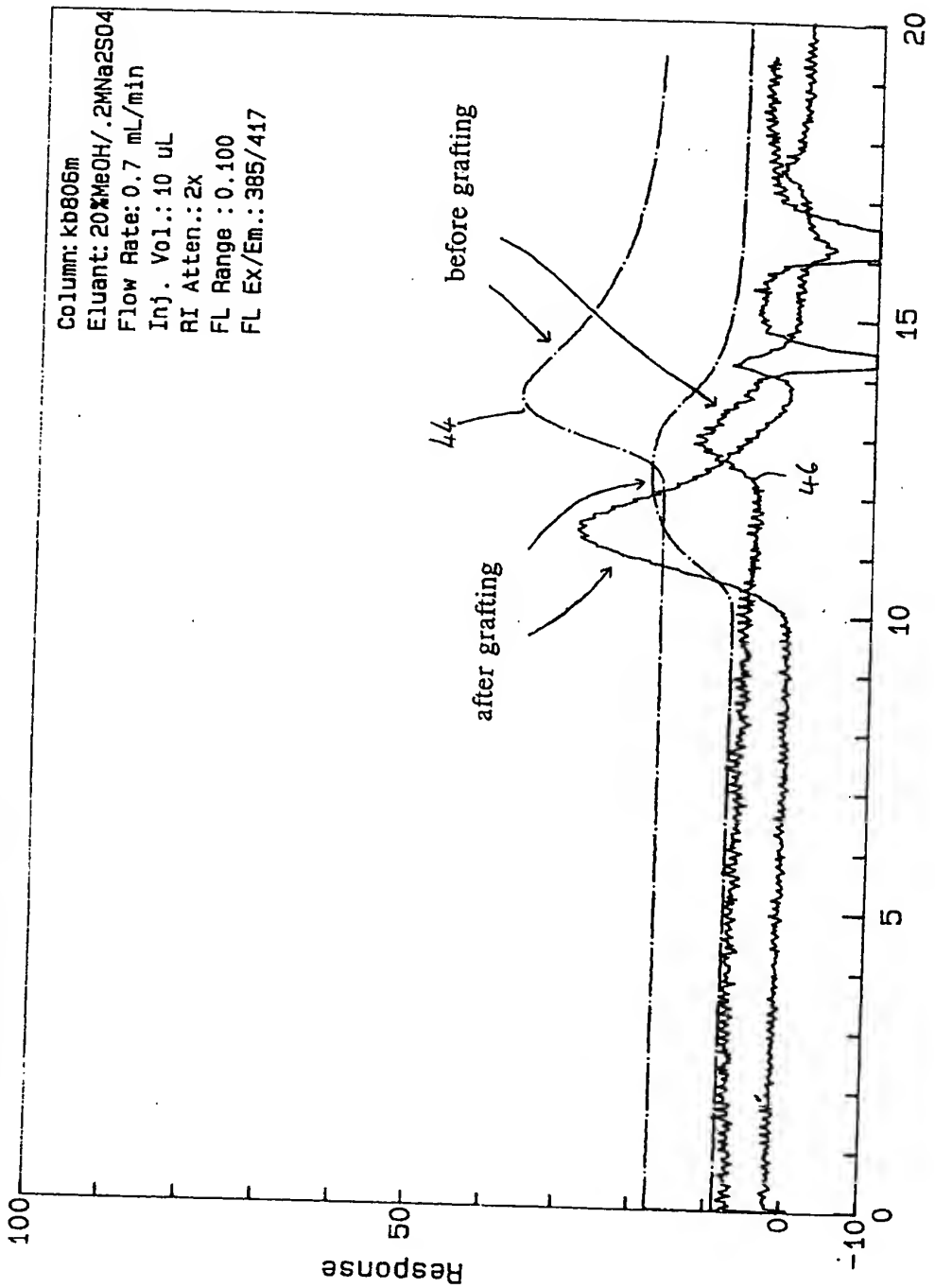


Figure 10: GPC chromatogram for AT-labelled PSSS (46000 g/mol) before and after grafting of SSS side chains (SSS/80% ethylene glycol/135 °C/5h). Polymers were reacted with fluorescamine prior to analysis. Signals from RI (purple) and fluorescence (red) detectors are shown.